EXPERIMENTS AT HIGH TEMPERATURES AND PRESSURES.[1]

WITHIN a few miles of this lecture-room there is an unexplored region—to approach it we should have to move vertically downwards. It has been suggested by Mr. Parsons[2] that it would be worth while to make a short expedition in this direction, but the journey would be slow and the cost high—for instance, to bore a hole twelve miles deep was estimated to be a labour which would occupy eighty-five years and cost 5,000,000*l*. A well-to-do man desiring to benefit his fellow creatures could not do better than undertake this project, but until he comes forward we must perforce be content to try to imitate in our laboratories the temperature and pressure conditions which would be met with deep down in the earth.

Information, attainable from experiments under these conditions, is essential to the development of any exact concept of the structure and evolution of the earth. One of the most important questions in connection with the study of bodies under high pressures and at various temperatures is as to whether any particular body is solid or liquid under specified conditions, and, if solid, whether it is amorphous, glassy, or crystalline. That pressure would influence the melting point of solids was clearly put forward by Clapeyron in 1834, but it was not until after the establishment of the mechanical theory of heat in the "forties" of the last century that the exact numerical relations could be established, as was done by Prof. James Thomson in 1851, when he calculated, for the first time, the amount by which the temperature of fusion of ice would be reduced by a given increase of pressure. The ideas underlying such calculations are based on a consideration of the way in which heat is converted into mechanical work in any prime mover depending on a heat-supply, and were first formulated by Carnot in 1824, before the true nature of heat was understood. As the matter is fully dealt with in every textbook, I will merely remind you that Prof. James Thomson was able to obtain an equation between the mechanical work actually produced under stated conditions and the work which, according to Carnot's principle, must be developed by a reversible engine operating between fixed temperature limits upon a given amount of heat.

The general relation for a substance undergoing a change of state at absolute temperature T, such change involving a change of volume Δv and an absorption or emission of heat at constant pressure Q_p, is, reserving the question of sign,

$$\frac{dT}{dp} = \frac{\Delta v T}{Q_p}$$

or, in words, the change of melting point produced by unit change of pressure equals the product of the absolute temperature, and the ratio of the change of volume of unit mass on melting to the quantity of heat absorbed or emitted by unit mass in the process.

Now the greater number of substances when they pass from the liquid to the solid state evolve heat and contract in volume. An increase of volume is, of course, a positive quantity, and if heat is absorbed during this increase it is reckoned positive also. In the case of water, heat is evolved during freezing as in other cases, but the mixture of ice and water has a smaller volume than the solid ice. Accordingly, the change of volume in this case is negative, and the melting point falls as the pressure rises.

The first fairly exact confirmation of the theory appears to be due to De Visser,[3] who selected acetic acid most carefully purified as a test substance, though valuable experiments up to much higher pressures had been previously made by many others, particularly by Dewar on water,[4] Ferche on benzol,[5] and Damien[6] on a variety of substances.

It is necessary to work with a pure substance in order to test the theory, or at all events with one the solid phase of which has the same constitution as its liquid phase. If the acetic acid had not been pure, the probability is that the frozen part would have contained more or less of the impurity than the unfrozen, and consequently a state of affairs not contemplated in the theory would have arisen. From the experimental point of view, it is obvious that a sharp melting point is a necessary condition for its accurate observation.

A quantity of acetic acid—rather more than 40 c.c.—is confined by mercury in a closed apparatus based on a previous design by Bunsen, which also contains air in a graduated tube. When the acetic acid melts it expands, and compresses the air through the intermediary of the mercury, whereby the pressure can be inferred. The part of the apparatus containing the acetic acid is immersed in a bath which can be kept at any desired temperature. As the melting progresses a pressure is set up by the expansion, and finally attains such a value that no further melting can take place. We then have a mixture of solid and liquid acetic acid in presence of each other under a measured pressure and at a known temperature. The quantities entering into the calculation are ascertained from other experiments—notably the ratio of the change of volume to heat absorbed was ingeniously ascertained by a modification of Bunsen's ice calorimeter. The final result was that the rate of variation of temperature of melting point with increasing pressure was calculated to be 0·02421° C. per atmosphere as against 0·02435° C. found by experiment, a difference of 0·57 per cent. I have dwelt on this work at some length in the hope that it may make the nature of the problem clear. It is to be noted that the experimental difficulties are considerable, and are enhanced by the fact that we have no *a priori* reason to suppose that the rate of change of melting point with pressure is a constant quantity independent of the pressure. In fact, it was shown by Sir Joseph Thomson about 1886[1] that in calculating the change of melting point we ought to take into consideration "the difference between the energy due to strains produced by the pressure in unit mass before and after solidification." Sir Joseph Thomson's reasoning, based as it is on a generalised Lagrangian method of treating problems involving energy changes, is unsuited for discussion in a non-mathematical address, but it is easy to see that if the compressibilities of liquid and solid are different, then the change of volume accompanying the change of state of unit mass must itself depend on the pressure, and therefore the pressure change of melting point, which is proportional to the change of volume, must depend on the square of the actual pressure so far as this part of the effect is concerned. This anticipation was realised by Damien in 1891, who showed that the melting points of substances in terms of the pressure could be expressed by a formula of the kind

$$t = t_0 + a(p-1) - b(p-1)^2,$$

t_0 being m.p. under 1 atmosphere pressure.

I think we may add that there will also be a small effect depending on changes of energy in the capillary layer separating the phases.

The first adequate investigation of the change of m.p. under pressure over a wide range of pressures was made by Barus.[2] Time does not permit me to do more than exhibit the results obtained, though the apparatus employed was most cleverly designed. It requires great experimental knowledge and ingenuity to infer with accuracy changes of volume of a few per cent. of the original volume at pressures of 1500 atmospheres, nearly ten tons per square inch. If we note the pressures and temperatures of melting, and plot the result as a curve against the pressure and temperature, we obtain what is called a melting-point curve, and this divides the field into two parts, so that on one side of the curve the temperature and pressure at each point have such values that the substance is solid, while on the other side their values are such that the substance is liquid. It is instructive, therefore, to regard the melting-point curve as the line separating the region of solid from the region of liquid. Along the line, and along it only, *i.e.* at the pressures and temperatures indicated by points on the line, the solid and liquid phases can exist in equilibrium together. Such a diagram is called a "diagram of condition."

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[1] Discourse delivered at the Royal Institution on Friday, March 19, by Richard Threlfall, F.R.S.

[2] B.A. Reports, Cambridge, 1904, 672.

[3] Recueil des Travaux Chimiques des Pays Bas xiii., 1893, 101.

[4] Proc. R.S., xxx., 1880, 533.

[5] Wied. Ann., xliv., 1891, 265.

[6] C. R., cxii., 1891, 785.

[1] Applications of Dynamics to Physics and Chemistry, 259.

[2] Bulletin No. 96 of the U.S.A. Geological Survey, 1892.

By far the greater part of our information as to the quantitative relations of bodies at high pressures we owe to Prof. Gustave Tammann, who has collected his results in a book entitled "Kristallisieren und Schmelzen," the advent of which (1903) must be regarded as an important event in the history of the subject.

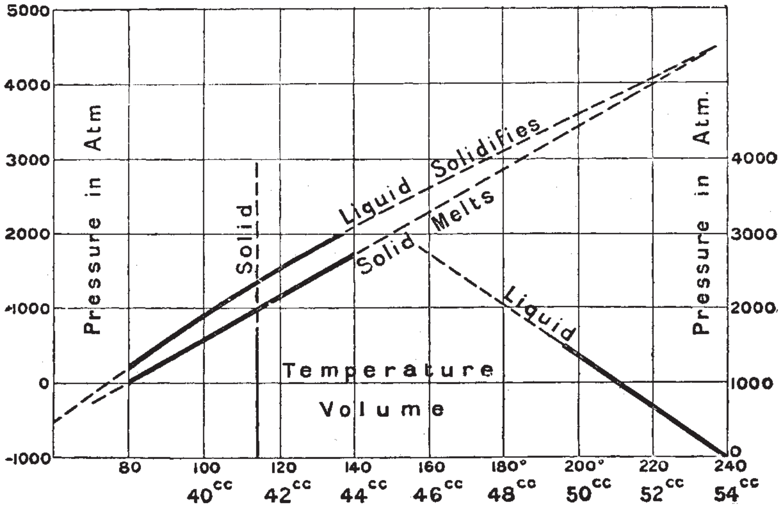

FIG. 1.—Full lines indicate part of field actually explored. Dotted lines indicate extrapolations.

The complete thermodynamic specification of a body involves a knowledge of its mass, volume, pressure, temperature, energy, entropy, surface tension, and nature, whether liquid, solid, glassy, crystalline, or amorphous.

Prof. Tammann has simultaneously measured the pressure, temperature, volume, and mass of many substances under high pressure, and at temperatures extending from 80° C. to 200° C.—taking cognisance of the physical state—and has thus been able to plot out many interesting diagrams of condition. The apparatus consists of a screw press by which a piston of ebonite is driven down a steel cylinder of small known cross-section. The cylinder is filled with oil, and the ebonite piston fits practically oil-tight. The oil communicates with the oil contained in a strong steel vessel, which also encloses a glass tube open at the lower end, containing the substance and dipping below the level of mercury contained in a dish. The oil occupies the rest of the space. The steel vessel is placed in a thermostat so that its temperature can be ascertained. The oil pressure is measured by a Bourdon gauge, which it was possible to standardise, thanks to the previous work of Amagat and Tait. In order to construct a diagram of condition, it is necessary and sufficient to find a number of points separating the liquid from the solid area, or separating the areas corresponding to different crystalline forms in the case where the transformation of one sort of crystal into another is under investigation. To understand how this is done, it is best to take a special case. If we have a quantity of a substance under a known pressure and temperature in the piezometer, and suddenly increase the pressure, so that there is not time for heat to pass in or out to any appreciable extent before the pressure gauge can be read, we have practically adiabatic compression. If the apparatus be then left to itself, the heat which we may suppose to be liberated by the pressure will slowly diffuse outwards, and the pressure will fall as time goes on. If we happen to start from a point on the m.p. curve before the pressure is raised, then the final result will be that we shall thaw or freeze more or less of the material, and the original pressure will be exactly regained, the change of state compensating the impressed change of volume. If, however, the increase of pressure has been so great that a change of state of the whole mass has been brought about, then the after variation of pressure will be so much greater that it is easy to distinguish this case from the previous one.

The accompanying diagram (Fig. 2), taken from Prof. Tammann's book, shows how the equilibrium curve can be located in the case of carbon dioxide and naphthalene. In the former case the temperature was 0·31° C. The pressure was 3800 kilograms per sq. cm., or 24·13 tons per sq. inch. (157·49 kilograms per sq. cm. = 1 ton per sq. inch = 152·38 atmospheres.)

The pressure was raised adiabatically to 4400 kg./cm.^{2} (27·93 tons/sq. inch), and the subsequent fall of pressure plotted against a time scale for ten minutes. The pressure was then adiabatically reduced to 3550 kg./cm.^{2}, and the recovery curve again plotted. The equilibrium pressure must lie between the pressures approached asymptotically on the diagram, *i.e.* between 3825 and 3792 kg./cm.^{2}. A repetition between narrower pressure limits enables the pressure to be fixed at between 3808 and 3797 kg./cm.^{2}. A similar procedure fixed the pressure of the m.p. of naphthalene between 3090 and 3080 kg./cm. at the temperature considered, a difference which corresponds to 0·2° C., the actual temperature possibly differing from the thermostat temperature by 0·1° C.

We may now pass on to the consideration of some of the results obtained, which refer, not only to change of melting points, but to changes in the temperatures of transformation of isomorphic forms.

As illustrations of such changes, I show here the transformation of yellow to red mercuric iodide, which shows well in the projection microscope; also Mitscherlich's transformation of potassium bichromate, and sulphur in two forms.[1]

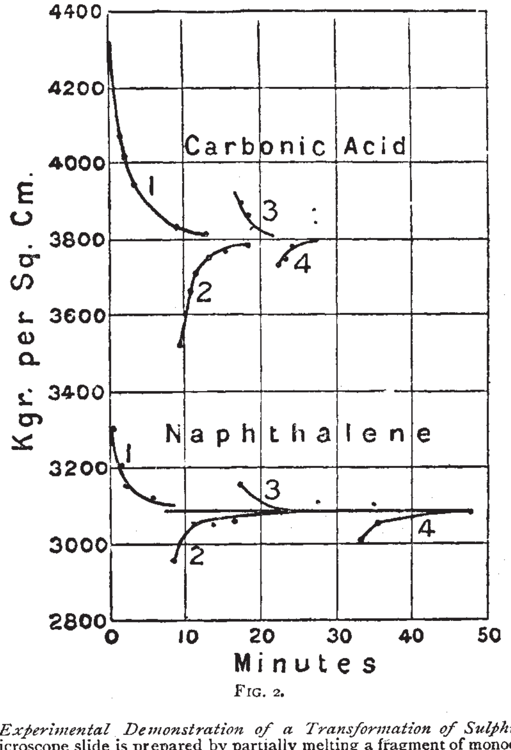

FIG. 2.

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[1] *Experimental Demonstration of a Transformation of Sulphur.*—A microscope slide is prepared by partially melting a fragment of monoclinic sulphur, and enclosing some of the melt between the slide and cover-slip, well pressed together. The presence of unmelted monoclinic sulphur insures the crystallisation of this variety on lowering the temperature. By means of a hot stage it is possible to preserve the crystallisation long enough to exhibit it by means of a projection polarising microscope. The appearance is very characteristic. Another slide is prepared, but this time all the sulphur is melted, and can generally be undercooled so far that it crystallises in what

The case of sulphur is one of great interest. It has long been known that sulphur can exist in at least three solid forms. It crystallises from some solvents in octahedral crystals, from others or from its liquid state in monoclinic crystals. In the latter case some amorphous sulphur is generally dissolved in the crystals, and the amorphous variety itself is formed in tough vitreous masses when molten sulphur, heated until it becomes very viscous, is poured into cold water. At ordinary temperatures the octahedral form alone is stable. It has been found that at atmospheric pressure octahedral sulphur is converted into monoclinic at 95·4° C., and in the process 2·7 gram-calories per gram of sulphur are evolved. The density of octahedral sulphur is about 2·03 and of monoclinic about 1·98 at ordinary temperatures. In accordance with the principles developed previously, the transformation temperature of rhombic to monoclinic sulphur must rise with increase of pressure. So far back as 1887 Roozeboom[1] was able to predict that the diagram of condition for sulphur would be as shown in Fig. 3.

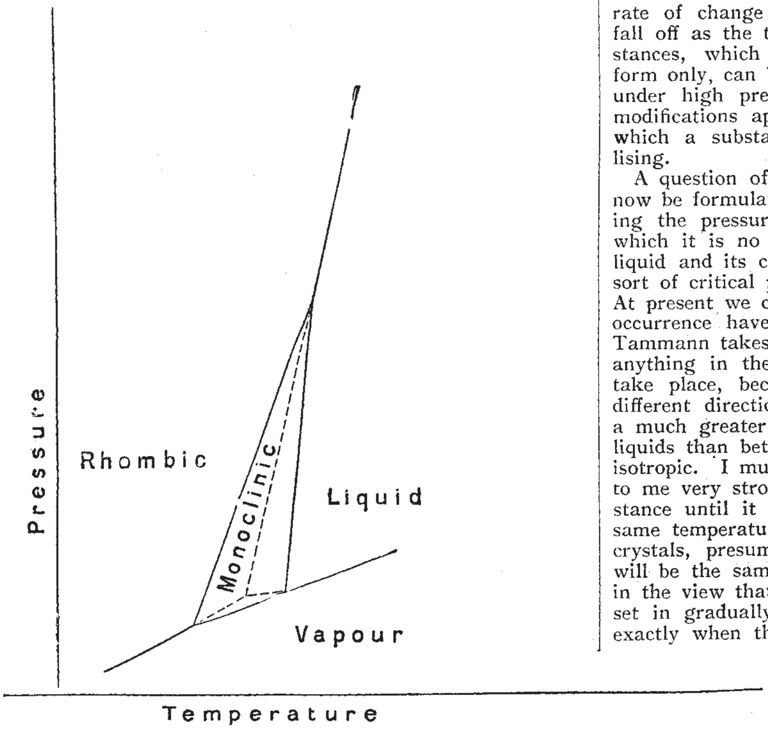

FIG. 3

Prof. Tammann has supplied the corroboration of the existence of the triple point.

Suppose that we have sulphur at a pressure of about 1500 kg./sq. cm. (9·52 tons/sq. inch) and raise its temperature to about 160° C. or more, we shall cut the melting-point curve of octahedral sulphur, and the sulphur will melt. If we then allow the sulphur to cool, keeping the pressure up, octahedral sulphur will crystallise from the melt instead of monoclinic sulphur. This very likely has some bearing on the occurrence of native crystals of octahedral sulphur.

It is not every substance which has such sharply defined properties as sulphur, though even these are not so sharp as they might be, owing to the constant presence of amorphous sulphur. An instructive case is afforded by phenol. As the diagram shows, there is a considerable region of the field in which two kinds of crystals of different density can exist together, the curves forming the boundary of this region of pseudo-equilibrium.

It may be that the two crystalline forms of carbon which apparently can exist together indefinitely at ordinary temperatures and pressures are an illustration of the same property.

As a final illustration we may note the results for water down to −80° C., from which it appears that it possesses three allotropic crystalline forms with at least two melting points.

The melting curves of from thirty to forty substances have been investigated, mainly by Tammann, up to about 3000 kg./sq. cm. = 19·05 tons/sq. inch, and the general result has been to show that there is a tendency for the rate of change of melting temperature with pressure to fall off as the temperature rises, and also that many substances, which at ordinary pressures crystallise in one form only, can be caused to assume allotropic modifications under high pressure. This tendency to form allotropic modifications appears to be associated with the extent to which a substance can be under-cooled without crystallising.

A question of the greatest interest and importance may now be formulated, What will happen if we go on increasing the pressure? Will a state of affairs be reached in which it is no longer possible to distinguish between the liquid and its crystalline form? Will there be, in fact, a sort of critical point at which the melting curve will end? At present we can only say that no indications of such an occurrence have been observed experimentally, and Prof. Tammann takes the point that it is highly improbable that anything in the nature of continuous transformation can take place, because a crystal has different properties in different directions related to its axes, and there is thus a much greater qualitative difference between crystals and liquids than between liquids and gases, both, of which are isotropic. I must admit that this argument does not appeal to me very strongly. If it be possible to compress a substance until it reaches a state in which, at one and the same temperature, the liquid has the same density as the crystals, presumably the mean distance of the molecules will be the same in both cases. I see nothing monstrous in the view that in these circumstances crystallisation may set in gradually, and that it may not be possible to say exactly when the liquid ceases to be a fluid and becomes a crystalline solid. There are no theoretical or other grounds for supposing that the phenomena of crystal growth, as observed when there is a change of volume accompanying the crystal formation, will necessarily hold when no such change of volume occurs.

If we refer to the theory of the change of m.p. by pressure it is obvious that if either the change of volume or the latent heat of melting vanish at any temperature or pressure on the melting curve, then in the neighbourhood of this pressure the curve must degenerate to a point, or small pressure changes will not affect the m.p. It was pointed out, however, that there is a term or terms depending on the square of the pressure, and if these were relatively important the only thing we should notice would be a change of curvature at the point under consideration. It does not follow that there is no maximum or minimum to the melting temperature of any particular substance because the term in P^2 may be vanishingly small; it may be (and generally is) of opposite sign to the term in P, and in this case it is only a question of the relative importance of the terms where the maximum or minimum melting point lies. Damien's empirical formula expresses precisely the effect to which I refer. The practical result which is of importance in questions affecting the condition of the inner layers of the earth is that we are not entitled—in fact, it is wrong—to suppose that pressure must necessarily go on raising the melting point indefinitely; everything depends on the substance under con-

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is believed to be the octahedral system. This slide is then placed in the projection microscope, when it is seen that its appearance is totally different from that of the first slide. The preparation of octahedral sulphur is then heated on the hot stage, and when the transformation temperature is reached it is seen that the structure begins to change—the crystallisation breaks up and becomes granular, the granules showing in general much more colour than the original crystallisation. These granules are taken to be monoclinic sulphur. The temperature is now raised until about half the preparation has melted, and it is then allowed to cool back a little so as to crystallise. The crystals now show the characteristic monoclinic crystallisation with brilliant colours, since unmelted monoclinic sulphur is present.

[1] Rec. Trav. Chim. Pays-Bas, vi., 1887, 314.

sideration. It is therefore necessary to make such experiments as those of Tammann at vastly higher temperatures and pressures than those we have been considering, up to probably more than 10,000 kilograms per sq. cm. (or 63·5 tons per sq. inch).

In 1893 some experiments were described by Parsons[1] in which carbon rods were heated by electricity under a pressure usually of 15 tons per sq. inch, but rising in one case to 30 tons per sq. inch. The pressure was obtained by means of a hydraulic press, but no detail is given.

I have been desirous for many years of making some experiments at high temperatures and pressures, but for a long time could think of no way of ascertaining the pressure at temperatures over a red heat except by the use of compressed gases. In 1902 Sir Andrew Noble was kind enough to have some drawings prepared for a wire-wound steel pressure vessel to carry a pressure of 50 tons per sq. inch. The pressure was to be supplied by a compressed gas, and some details of the heating arrangements were designed, when a calculation of the cost of the gas compressors, vessel and appurtenances, made it clear that the undertaking would be beyond my means. I then endeavoured to find a simpler form of apparatus, and finally was led to contemplate the substitution of graphite for compressed gas, Spring having pointed out that crystalline graphite flows very easily at high pressures. A simple trial made it clear that the graphite of Ceylon does, in fact, possess the property of flowing like a liquid under high pressure to a sufficient degree to allow of pressure being transmitted by it. Graphite can be used, with some reservations, to transmit a pressure just like water or oil, though it is, of course, inferior in fluidity, and, as I have now discovered, occasions a loss of "head" which is not independent of the pressure itself. My former statement in the Chemical Society's Journal, 1908, is erroneous, though the results of the experiments are, I believe, hardly, or not at all, affected by the mistake, for a reason which will be clear later on. After several trials, the apparatus which I have here to-night was evolved, and some experiments were made with it. These experiments are not of any great importance, and, indeed, I feel almost ashamed of bringing them to your notice—I can only say, in excuse, that everything must have a beginning.

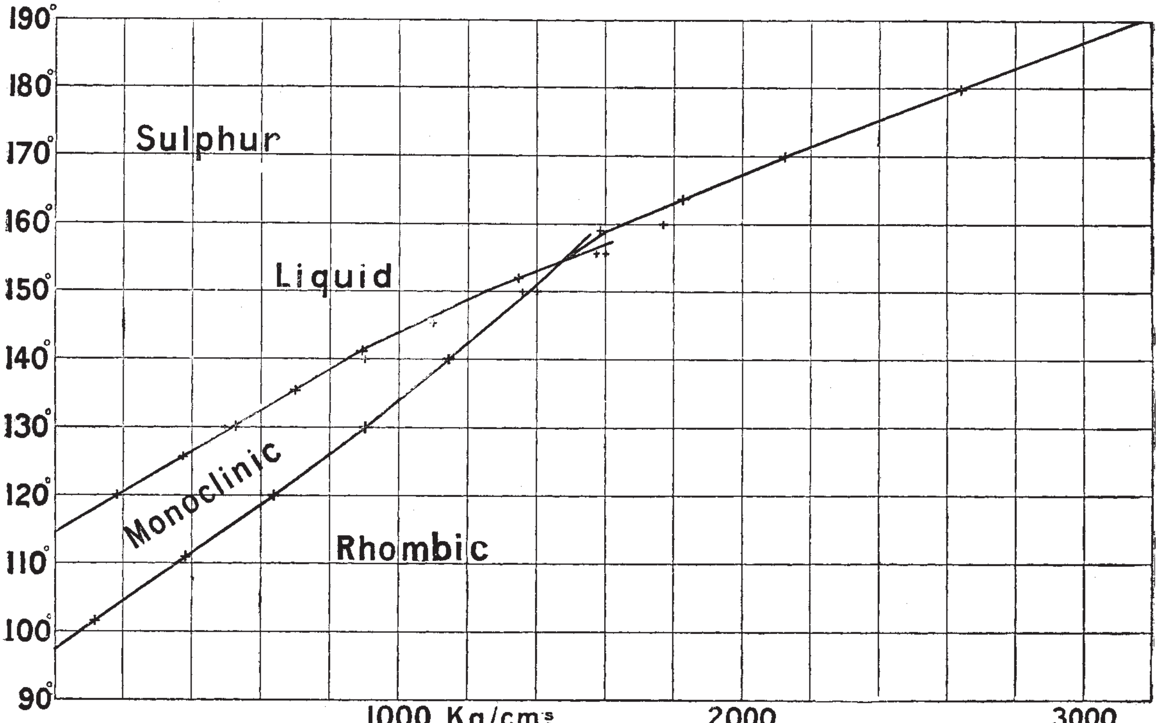

FIG. 4.

I believe, however, that the apparatus is sufficiently simple, cheap, and effective to enable others with more leisure at their disposal to make a beginning of an investigation of the properties of matter up to 100 tons per sq. inch, and at temperatures up to about 2000° C. At present, however, it is not possible to infer with accuracy the volume of the substance under these extreme conditions, nor can its physical condition be more than approximately and indirectly inferred—we must content ourselves with the production of transformations which we can make persist down to ordinary temperatures and pressures.

If we refer again to the sulphur diagram, we shall see how this possibility may arise. If sulphur is melted and cooled slowly, monoclinic crystals are found—when the temperature sinks below 98° C. these crystals undergo spontaneous transformation to the rhombic form—but all that we see is that the monoclinic crystals become opaque; the external form of the crystals is still monoclinic, but they are merely pseudomorphs of the original crystals. To obtain large octahedral crystals we may suppose that we begin by melting sulphur and raising the temperature and pressure until the former stands at 160° C. or over, and the latter at not less than 1600 kg./cm.^{2} (10·16 tons/sq. inch).

If we then slightly reduce the temperature or raise the pressure, we shall have the crystallisation of the sulphur in the rhombic form. By maintaining the pressure as the mass cools, and when it is cold releasing the pressure, we should finally extract rhombic crystals. To this we may, of course, add that we need not expect crystals of any size unless we cool at the proper rate. It appears that there are at least two phenomena requiring attention in relation to the production of crystals—one is the relation between the amount of undercooling necessary to induce spontaneous crystallisation, and the other is the rate at which the crystals will grow when they have once started. If we want large crystals we must not have an excessive number of points of spontaneous crystallisation, nor must we have too high a rate of crystal growth or the crystals will by all experience tend to be felted together. The temperature condition giving birth to the most favourable number of spontaneous centres is not necessarily the temperature at which crystals grow to the largest size, so there is really no escape from finding by direct trial the most effective way to go to work.

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[1] Phil. Mag., xxxvi., 304.

Another possibility is brought to light by an examination of a case of pseudo-equilibrium, such as that of phenol. Here we have three regions—in one No. 1 alone is stable, in another No. 2, and in the third both Nos. 1 and 2 are stable. The case of iodide of silver is similar but more complicated. If in the area C we change the pressure, the temperature remaining constant and the material consisting of a mixture of the two stable phases, we can alter the proportions in which these phases exist, but we cannot cause either of them to disappear.

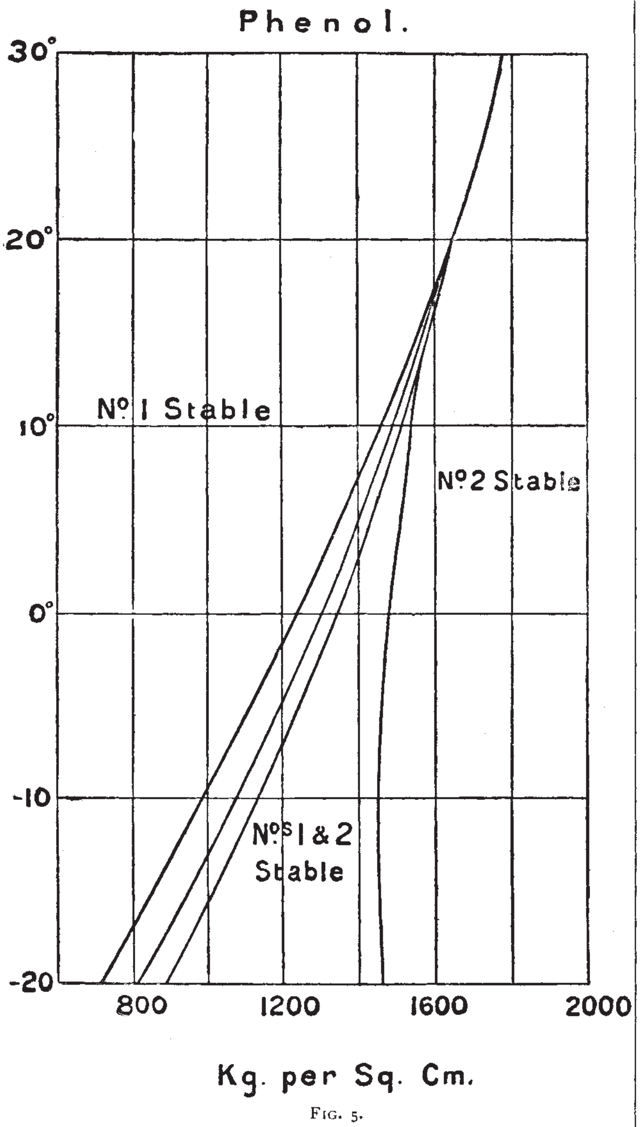

FIG. 5.

A notable case of this kind is that of graphite and diamond, both perfectly stable in presence of each other at atmospheric pressure up to a temperature nearly that of the electric arc, say about 3000° C. If there be any similarity between the carbon and phenol diagrams, diamond would correspond to variety No. 2 of phenol and graphite to variety No. 1, heat being evolved in both cases when the less dense modification changes into the denser. If we desire to obtain phenol 2 from phenol 1, we note that, down to a temperature of $-20°$ C., we should require to keep the pressure always above about 600 kg./cm.^{2}, otherwise the operations would be similar to those described in the case of rhombic sulphur.

Similarly, to convert graphite to diamond on this analogy we should have to raise the temperature and pressure together to some unknown values, and then let the product cool, keeping up the pressure meanwhile.

The apparatus which I have used in making the experiment is based on the transmission of pressure by crystalline graphite or the softer metals. In order to ascertain how much pressure is lost during transmission, I have arranged an apparatus in which the material to be tested is exposed to a known pressure, tending to force it through a cylindrical space, identical in figure with the space in which the heating is intended to be carried out. The pressure transmitted is transferred by a simple device to a piston with a hard steel point, and this is forced by the pressure to penetrate a soft steel plate. In a subsequent experiment the same piston is forced by a known pressure into the same steel plate so as to penetrate to the same depth as in the main experiment. It is then possible to compare the pressure transmitted with the pressure applied.

Experiments of this kind have been made with lead and with graphite as pressure-transmitting substances.

So far as I know, there is no substance other than graphite combining the property of a certain amount of fluidity with the capacity to resist high temperatures, and our hope of studying chemistry at really high pressures and temperatures appears at present to depend largely upon it. It is true that some attempts have been made to use compressed gases, but the apparatus is vastly more complicated, and the experiments themselves become really dangerous in view of the immense potential energy possessed by gases at pressures of 100 tons per square inch. As illustrating this, I may mention that 100 tons per square inch is about the highest instantaneous pressure noted by Sir Andrew Noble in his well-known experiments on the exploding of cordite in closed vessels. The density of nitrogen at 100 tons per square inch is, taking Boyle's law as a very rough approximation, 15,240 times its density under standard conditions. This works out to rather more than 19, *i.e.* about the same as gold, and the energy stored is of the same order as that contained in an 'equal' volume of cordite, though its availability is lower.

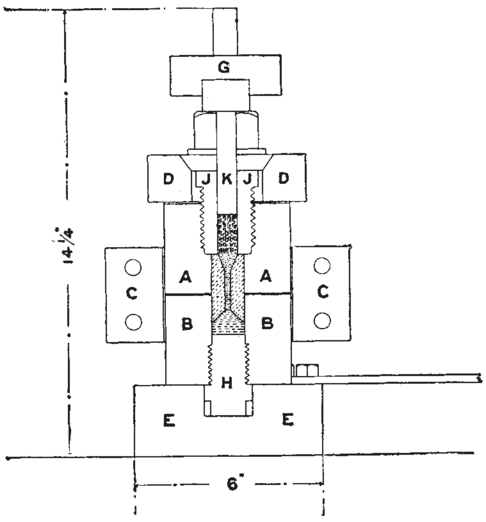

FIG. 6.

The construction of the apparatus I have used can be easily followed from the drawings. It consists essentially of a steel cylinder divided perpendicular to the longitudinal axis by a thin plate of mica, the two halves being clamped tightly together by an insulated ring and clamps at top and bottom. Pressure can be applied by an ordinary hydraulic lifting jack—the one I have used will lift fifty or sixty tons—the bore of the hydraulic cylinder being about 4½ inches. In order to operate at a high temperature it is necessary to line the cylinder with some refractory substance, and I have generally used magnesia for this purpose, though zirconia or thoria might be better. Purified magnesia is first melted in an electric furnace, and then ground in an iron mortar until it is very fine. The powder is freed from iron as well as possible by a strong magnet, and after being sifted is pressed into the cylinder little by little by hydraulic pressure so as to form a solid plug. This is then bored out with a hard steel drill to the required diameter. In pressing magnesia I have found that it is not possible to thoroughly consolidate the powder in greater thickness than a few millimetres, even under a pressure of 50 tons per square inch. In fact, magnesia is a substance which appears to be almost devoid of the fluid properties so marked in graphite—an essential condition for its use in the apparatus. I have tried various other linings, ground flint, alumina, &c., but they have no advantage over magnesia, and are even more difficult to drill out. Alumina prepared from the crystalline hydroxide is very easily compressed into cakes, and makes a good lining, but it is too fusible for experiments on carbon, and is probably more easily reduced. The cylinder having been lined, the bottom is filled in with Acheson graphite in electrical communication with the base of the apparatus. The substance to be operated upon is placed in the narrow part of the bore, and packed in with graphite or lead if that is suitable. The pressure is applied by a ram of hardened high-speed steel working upon a reservoir of graphite or lead contained in the plug closing the cylinder at the top and electrically connected to the other terminal of the supply. The chief uncertainty in regard to the pressure which actually reaches the subject of the experiment lies in the possibility of the ram being held to some extent by friction against the sides of the cylindrical hole in which it works, and in the consolidation of the graphite, with reduced fluidity, before it actually flows. One has to trust either to the hardness of the ram or to leave a space round it sufficient to allow graphite to escape, when the apparatus follows the lines of Amagat's standard pressure gauge, but the duration of the experiment is curtailed by the exhaustion of the graphite supply. A correction has to be applied for the pressure absorbed by the lead or graphite in accordance with the results of the preliminary trial. It is fair to say that no tendency of the ram to stick has ever been noticed—on the contrary, changes of volume brought about by heating have made themselves evident at once on the pressure gauge of the hydraulic press.

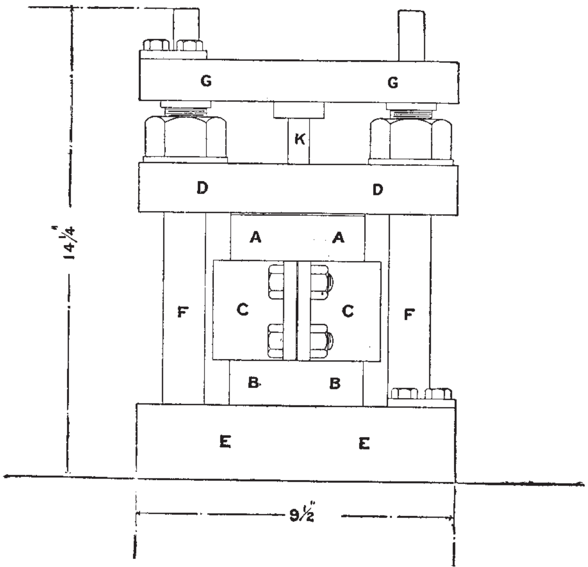

FIG. 7.

When working with any form of carbon there has been no trouble in arranging to heat the body which is being compressed by electrical means. It has been found most convenient to adjust the current to about the value required by means of a resistance—large compared with that of the pressure vessel—the latter being short-circuited meanwhile. In making an experiment, the hydraulic press is worked until the desired pressure is attained, and then by opening the switch the current is thrown on to the apparatus. When the magnesia lining begins to melt, the pressure, as shown by the pump gauge, is seen to fall, graphite flows into the magnesia tube, and the pump is worked so as to compensate for this. Under these conditions the pressure is probably transmitted without appreciable loss, as the narrow part of the cylinder is now in a fluid bath. After a sufficient time has been allowed the switch is closed, and the pressure kept up by pumping until the apparatus is cold. Originally an apparatus with a cylinder made in one piece was employed, and in this case there was a considerable voltage between the graphite entering the apparatus and the steel walls of the pressure vessel. After a few seconds of intense heating it frequently happened that an explosion took place, due (as could be seen by subsequent examination) to filaments of graphite being driven through the magnesia and producing short circuits against the steel vessel. With the construction above described these explosions do not occur, and there is the additional and very real advantage that when an experiment is over the apparatus can be opened in the middle and everything exposed to view.

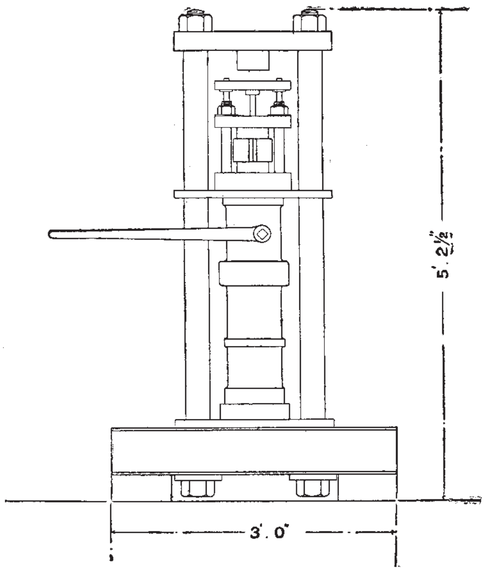

FIG. 8.

A large number of experiments were made on different kinds of carbon and graphite. The weight of material in the highly heated part was generally from 1 to 2 grams, and the energy supply was at a rate of 5 to 10 kilowatts for from three to six seconds. The pressure in a successful experiment lay at from 50 to 100 tons per square inch throughout. The magnesia lining was usually melted for a distance up to 1 centimetre round the graphite. Now magnesia melts at ordinary pressures at about 2000° C., but the energy supply is sufficient to render it possible that temperatures of from 3000° to 4000° C. may have been reached; it is possible that about 3000° C. was actually attained at the centre of the charge. The results obtained were uniform. No matter what form of carbon (excluding diamond, which was not tried) was packed originally in the apparatus, the final product was soft, well-crystallised graphite, which agrees with some results of similar experiments described by Mr. Parsons,[1] but not with the results claimed by Dr. Ludwig.[2]

In several experiments the crystalline mass of graphite was tested in regard to its porosity, and this was found to be considerable—a remarkable result, having in view the conditions under which it had been formed.

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[1] Proc. R.S., 79.

[2] Zeits. f [illegible] 1902, 273

Another point of interest was that where the soft graphite had been driven into the Acheson graphite plug at the bottom of the apparatus it became extremely hard, so much so that a hard steel file made little or no impression upon it.

The main difference in treatment of this part of the graphite as compared with the remainder is that it was cooled much more quickly, thanks to the high heat conductivity of the Acheson graphite plug. The cause of hardening has hitherto not met with any satisfactory explanation.

No appreciable quantity of carbide of magnesia was formed in the experiments. The magnesia close to the graphite core contained traces of carbides, but as there were always traces of iron left from the drilling-out process, this may be plausibly accounted for by the formation of carbide of iron.

The graphite was finally systematically searched for microscopic diamonds by Staudenmaier's modification of Brodie's method of conversion of graphite into graphitic acid,[1] or else by Moissan's modification of the same method.[2] A convenient means of distinguishing diamond in fine powder from most or all of the substances which are not separated by a liquid of density 3·34 at 4° C. is to heat the powder in a silver spoon to a dull red heat in fused potassium hydroxide. Check experiments showed that diamond dust easily passing a sieve with 100 threads to the inch would withstand the action of molten caustic potash at a temperature at which the edges of the silver spoon began to melt for five or ten minutes. Crystals of alumina or of carborundum are entirely destroyed by this fusion, but the diamond particles seemed to have undergone no change. In fact, the individual fragments could be recognised under the microscope after passing through the ordeal.

I am led to consider that my experiments indicate that no wholesale transformation of amorphous carbon or graphite into diamond can be brought about by temperatures of the order of 2000° C. and pressures of more than 50 and less than 100 tons per square inch. There is some uncertainty, as already mentioned, in regard to the actual pressures operative during the trials. Prof. Tammann has, however, obligingly directed my attention to the fact that the equilibrium curve graphite-diamond may nevertheless have been crossed, but that no diamond was formed because time for crystallisation was not allowed under the conditions of the experiment. I confess my idea in making the trials was that the amorphous carbon or graphite might be forced to melt, and then that the conditions would require it to re-crystallise as diamond—not, of course, in the form of large clear crystals, but rather in the form of bort or black diamond.

The experiments described have only been rendered possible by the invention of high-speed steel, which keeps its hardness up to nearly, or quite, a red heat, and any further advance—mainly in the direction of the allowance of more time—must wait for improvements in that material. It may very well be, however, that the limits of temperature within which crystallisation in diamond form can take place are really very narrow at any pressure; and in this case it will be a matter of very great difficulty to make an apparatus in which the conditions could be kept constant for a sufficient length of time, and the difficulty would be greater the higher the temperature.

It is noteworthy from this point of view that in Moissan's artificial production of diamond very much lower pressures and temperatures were used than those just described. I have shown[3] that, using iron as a solvent, it is highly improbable that Moissan attained a pressure of more than 20 tons/sq. inch, and when silver was employed the pressure must have been much lower. A similar criticism places the effective temperature of formation of diamond in iron or silver spheroids at something of the order of 1500° C. Comparing the experiments of Moissan with those described above, it looks as if Roozeboom's opinion is at present the most probable, viz. that solvents are necessary in order to depress the crystallisation point of diamond to a temperature at which the transformation to graphite is slow enough for rapid cooling to interrupt it. In this case the next step would be to repeat the experiments I have described at the highest possible pressure in the presence of iron, though Mr. Parsons[1] has already made some trials in this direction with negative results. We have, however, many metals which have never been tried in this connection, and one or other of them may turn out to have the requisite properties.

UNIVERSITY AND EDUCATIONAL INTELLIGENCE.

CAMBRIDGE.—The board of anthropological studies has elected Mr. A. R. Brown, fellow of Trinity College, to the Anthony Wilkin studentship in ethnology and archæology. The John Winbolt prize has been awarded to Mr. E. T. Busk, of King's College.

A university lectureship in zoology, recently held by Prof. Gardiner, is now vacant. The general board of studies will shortly proceed to appoint a lecturer to hold office from January 1, 1910, until September 30, 1914. The annual stipend is 50*l*. Candidates are requested to send their applications, with testimonials if they think fit, to the Vice-Chancellor on or before Saturday, November 27.

The Vice-Chancellor gives notice, on behalf of the board of geographical studies, that the Rev. T. G. Bonney, F.R.S., has consented to deliver a lecture in Cambridge on Thursday, November 25, at 5 p.m., on "A Desert Phase in the Development of Britain." By permission of Prof. Hughes the lecture, which will be illustrated by lantern-slides, will be given in the large lecture-room of the Sedgwick Museum of Geology.

The professor of botany also gives notice that Dr. H. H. W. Pearson, of Gonville and Caius College (professor of botany in the South African College, Cape Town), has consented to deliver a lecture at the Botany School on Friday, November 19, at 5 p.m., on "A Botanical Journey in South-west Africa."

The general board of studies has approved Dr. C. S. Myers, of Gonville and Caius College, and A. E. Western, of Trinity College, for the degree of Doctor in Science.

LIVERPOOL.—Mr. W. S. Abell, instructor in naval architecture at the Royal Naval College, Greenwich, has been appointed to the chair of naval architecture endowed by Mr. Alexander Elder.

OXFORD.—Mr. Balfour will deliver the Romanes lecture in the Sheldonian Theatre on Wednesday, November 24. Lord Curzon of Kedleston, Chancellor of the University, will preside.

SOCIETIES AND ACADEMIES.

LONDON.

Royal Society, November 11.—Sir Archibald Geikie, K.C.B., president, in the chair.—H. C. **Ross**: The vacuolation of the blood-platelets: an experimental proof of their cellular nature.—H. G. **Plimmer** and Captain W. B. **Fry**: Further results of the experimental treatment of trypanosomiasis, being a progress report to a committee of the Royal Society.—G. S. **West** and B. M. **Griffiths**: *Hillhousia mirabilis*, a giant sulphur bacterium.—Dr. H. B. **Fantham** and Miss Annie **Porter**: The modes of division of *Spirochaeta recurrentis* and *S. duttoni* as observed in the living organisms. The observations recorded were made on living Spirochætes. The examination of living material is imperative, as results based only on stained preparations are not always trustworthy. Both longitudinal and transverse division occur in Spirochætes, as seen in *S. recurrentis*, *S. duttoni*, *S. anodontae*, and *S. balbianii*. There is a periodicity in the direction of division exhibited by *S. recurrentis* and *S. duttoni*. At the onset of infection longitudinal division occurs. This is followed by transverse division of the

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[1] Ber., 1898, xxxi., 1485.

[2] Electric Furnace, 49, translation.

[3] Journ. Chem. Soc., xciii., 1908, 1351.

[1] *Loc. cit*